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Nanostructured Coatings with Self-Healing and Temperature Homogenization Functions for High Temperature Sliding Interfaces

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14. ABSTRACT

Within the present project, three different approaches to synthesize multifunctional low-friction nanocomposite coatings by sputter deposition have been explored, i.e. unalloyed ZrO_2 to investigate the effect of different deposition parameters on phase formation, ZrO_2 films with Ag addition, and finally ZrO_2 films with V addition. The knowledge on controlling phase formation during synthesis of ZrO_2 coatings by magnetron sputtering is the basis for the future exploitation of the stress-induced transformation of metastable ZrO_2 phases and for possible crack-stopping and self-healing mechanisms. While synthesis of Ag containing ZrO_2 films was hampered by formation of Ag clusters and agglomerates, the addition of V allows combining self-lubricious properties with strong endothermic reactions of phase-change materials suitable for reduction of local flash temperatures in tribological hot spots in the temperature range between 600 and 800°C. The project has contributed to a significant progress in widening the functionality and reliability of nanostructured coatings with added functionalities for highly loaded sliding contacts operated in broad temperature ranges.

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Nanostructured Coatings with Self-Healing and Temperature Homogenization Functions for High Temperature Sliding Interfaces

Final Report

1. Project Data

Project Title Nanostructured Coatings with Self-Healing and Temperature Homogenization Function for High Temperature Sliding Interfaces
Short Title Coatings with Self-Healing and Temperature Homogenization
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2. Project Goals

The objective of the project was to study basic and technological aspects of coatings for high temperature sliding interfaces, where the coatings show tailored multifunctional properties combining self-healing abilities and homogenization of local peak temperatures occurring in sliding contacts. The proposed project has been subdivided into three work packages: The first package is to synthesize coatings based on the zirconia phase with different alloying elements and contents by co-sputtering from pure and alloyed targets, work packages 2 and 3 are focusing on chemical/structural characterization and investigation of mechanical/ tribological properties and thermal stability.

Zirconia ZrO_2 exists in three different phases, where the transformation from the tetragonal to the stable monoclinic phase results in a volume expansion. One of the goals of this project is to investigate if this phase transformation occurring due to the localized stress field of a crack is suitable to enhance the toughness of the coating. Self-lubricious properties of the coating should be provided by a dispersion and/or solid solution of suitable elements providing low-friction properties over a wide temperature range. As a solid lubricant for room temperature, ReO will be used, while Ag and Au will provide for lubrication in an intermediate temperature range. For the temperature range above 500°C, we will use V_2O_5 which is expected to form a lubricious liquid film on top of the coating during high-temperature exposure. Melting of the V_2O_5 should occur due to high local flash temperatures in dry sliding contacts. Since melting of V_2O_5 is an endothermic reaction, it is expected that the energy to be consumed will result in a local decrease of contact temperature, consequently opening up new possibilities to control hot spots and to homogenize thermal gradients in sliding contacts.

The participating institutions in the project are the Department of Physical Metallurgy and Materials Testing of the University of Leoben (Montanuniversität Leoben, MUL, Austria) and the Air Force Research Laboratory (AFRL/RXBT, USA).

3. Experimental Details

All coatings for this work were deposited by a home-made pulsed dc reactive unbalanced magnetron sputtering device at the Montanuniversität Leoben, as shown in Fig. 1.

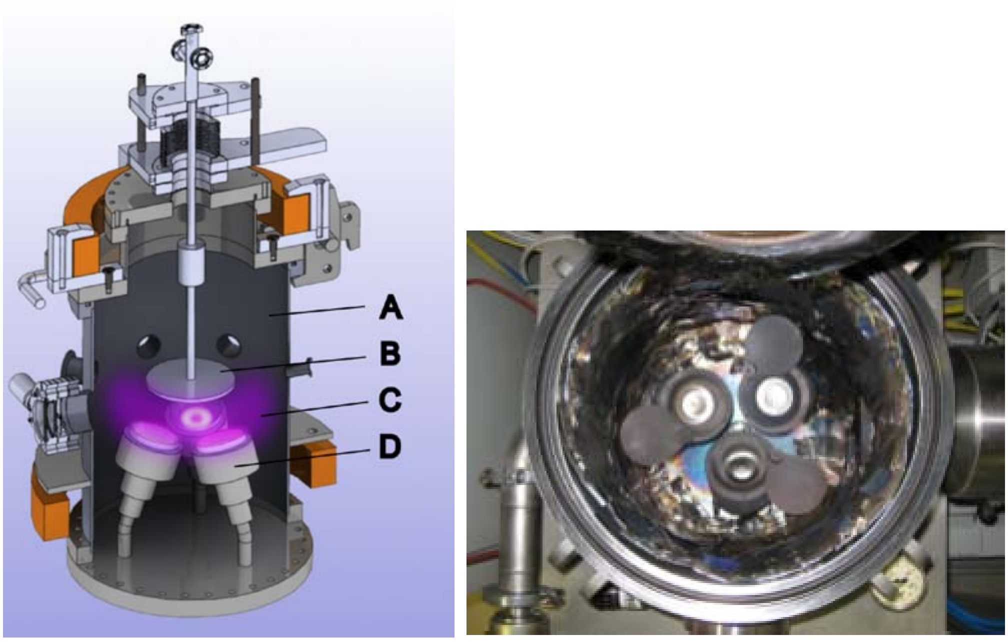

Fig. 3.1: Left: Schematic of the reactive unbalanced magnetron sputtering device used in this work showing the stainless steel chamber (A), the rotatable substrate holder (B), the plasma burning between substrate holder and magnetrons (C) and three magnetrons (D). Right: top-view into the deposition chamber with the three magnetron cluster.

The sputtering system consists of a cylindrical stainless steel chamber (Ø 380 x 235mm) (A) which houses a horizontal circular magnetron cluster with three water-cooled magnetrons (D). The magnetrons are radial swivel-mounted up to 18° inclined from their vertical position. Three 2" targets which are protected with air pressure controlled shutters are fixed on the magnetrons. The rotatable substrate holder (B) which is arranged equiplanar beyond the magnetron cluster in a distance of ~75mm can be heated up to 800°C. The Ar plasma (C) burns between the magnetron cluster and the rotable substrate holder. Two ENI RPG-50 (programmable frequency 50-250 kHz, duty cycle from 2.5 - 40 %) pulsed DC generators are used for the magnetron power supplies.

Two metallic Zr targets are supplied by one generator. The second generator supplies the third target (for this work, either a yttria-stabilised ZrO_2, a V or an Ag target). A third ENI RPG-50 generator is used for plasma etching of the substrates by applying a negative bias voltage. For vacuum generation in the deposition chamber a dual stage rotary vane pump and a turbomolucular pump are used.

All coatings were deposited on three different substrates: AlSI M2 high speed steel, Si (100) wafers, and Fe foil. M2 substrates which were quenched and tempered to a hardness of 65 HRC and afterwards polished were used for tribological tests. A further set of depositions was done on Si wafers for measuring the coating stress. For the DSC measurements, the coatings were synthesized on Fe foils to make a powder of the coating by dissolution of the foil in 15 % HNO_3. All substrates were ultrasonically cleaned in acetone and ethanol for 10 min and afterwards dried by hot air. The substrates were fixed on the substrate holder (see Fig. 1, B) which was mounted in the deposition chamber (Fig. 1, A). For further substrate cleaning, all substrates were plasma etched for 5 min at a temperature of 300°C after evacuation down to a total pressure of at least $1x10^{-5}$ mbar. Plasma was ignited between the substrate holder and the magnetrons using an Ar gas flow of 200 sccm which lead to a total pressure increase up to 10^{-3} mbar and by applying a negative bias voltage of -300 V to force bombardent of the substrate surface by Ar^+ ions. Afterwards, the heater was adjusted to a deposition substrate temperature of 500, 150 or 100°C for the synthesis of ZrO_2 based coatings without alloying elements, ZrO_2 films alloyed with V or Ag, respectively. The ratio of the gas flows of Ar and O_2 was kept constant at 30:10 sccm during all depositions for this work. The substrate holder was rotating all the time at maximum speed of 20 rpm. The deposition times were chosen so that all coating thicknesses were higher than 1 µm.

Coatings have been characterized with respect to their thickness (ball crater technique), adhesion (Rockwell C indentation test), morphology and topography (optical microscopy, scanning electron microscopy, SEM), chemical composition (energy-dispersive X-ray spectroscopy, EDX), microstructure (X-ray diffraction, XRD), stresses (cantilever beam technique up to 700°C in vacuum), hardness and elastic modulus (nanoindendation), friction and wear properties (ball-on-disc tests up to 700°C against alumina balls in ambient air), wear tracks (optical microscopy, SEM, optical profilometry, Raman spectroscopy), and microstructural changes occurring during thermal ramping up to 1000°C (differential scanning calorimetry DSC, thermogravimetry TGA, both in synthetic air, vacuum annealing up to 1300°C).

4. Results and Discussion

In particular, three different coating systems have been studied, (*i*) unalloyed ZrO_2 to investigate the effect of different deposition parameters on phase formation, (*ii*) ZrO_2 films with Ag addition, and (*iii*) ZrO_2 films with V addition. The research approaches based on adding of Re and Au had to be cancelled, because of the high costs of Re targets and because of the limited success with Ag addition, where similar results are also expected for Au. The main findings obtained within the mentioned three approaches are summarized in the following sections.

4.1 Control of phase formation during synthesis of ZrO_2 films by magnetron sputtering

The outstanding properties of ZrO_2 as a tough ceramics are based on its martensitic phase transformation from tetragonal to monoclinic. The ability to control phase formation during synthesis is therefore a prerequisite to exploit the full potential of this material. This has been investigated in detail for deposition of ZrO_2 coatings by reactive magnetron sputtering. Using metallic Zr targets in an argon/oxygen atmosphere, coatings showing the stable monoclinic ZrO_2 phase can be synthesized. Formation of the monoclinic phase occurs independent of substrate heating (up to 500 °C) and/or application of a pulsed bias voltage at the substrate (up to -100 V). To synthesize coatings of the high temperature tetragonal and cubic phases of ZrO_2, two different approaches have been investigated: doping with yttria and reactive sputtering in the presence of nitrogen.

For bulk synthesis, doping with rare earth metal oxides is a well known method to produce fully stabilized ZrO_2 in its cubic modification and also partially stabilized ZrO_2, which contains a mixture of the cubic and tetragonal phase. Here, a series of coatings with varying yttria content has been deposited by magnetron co-sputtering from two metallic targets and one yttria-stabilized ZrO_2 target in an argon/oxygen atmosphere. With this deposition setup, the whole range of phase compositions from monoclinic to tetragonal/cubic coatings via phase mixtures can be synthesized and the necessary yttria content to partially or fully stabilize the sputtered ZrO_2 coatings is determined. Fig. 2 presents a series of XRD patterns, where the Y content has been varied between 0 and 1.8 at.%, causing a change of the phase composition from monoclinic via a phase mixture to tetragonal.

An alternative method for tailoring the structure formation in reactively sputtered ZrO_2 films is the use of nitrogen as an additional reactive gas. It is not the incorporation of nitrogen into the coatings (i.e. no nitrogen could be detected within the coatings), but the target surface coverage with nitrogen that affects the structure formation. This allows for deposition of mainly tetragonal/cubic ZrO_2 coatings without significant amounts of additional elements in the coatings. Thus, not only structure formation can be controlled but also the reactive sputtering process is stabilized.

Finally, the thermal stability of the different microstructures synthesized has been evaluated by vacuum annealing treatments at 800 and 1300°C for 1 hour. Fig. 3 presents an overview of XRD patterns of ZrO_2 films with different Y contents after these annealing procedures. It turned out that the phase composition for all Y contents is stable at 800°C and changes to tetragonal after annealing at 1300°C. Similar annealing treatments done for the ZrO_2 films synthesized with nitrogen addition confirmed that the tetragonal/cubic phase mixture is stable also up to 1300°C. However, a change of preferred orientation of the tetragonal ZrO_2 phase from (002) to (110) takes place.

In summary, it can be concluded that ZrO_2 films have been successfully synthesized, and the main factors to stabilize different metastable and stable ZrO_2 modifications have been have been identified. Furthermore, the thermal stability of the metastable ZrO_2 phases has been explored. Attempts trigger phase transformation by mechanical loads (e.g. by nanoindentation) have up to now not been successful. The results obtained on controlling the phase formation during synthesis of ZrO_2 coatings by magnetron sputtering have been presented as a poster contribution at the International Conference on Metallurgical Coatings and Thin Films 2010 [1]; a manuscript is presently under preparation.

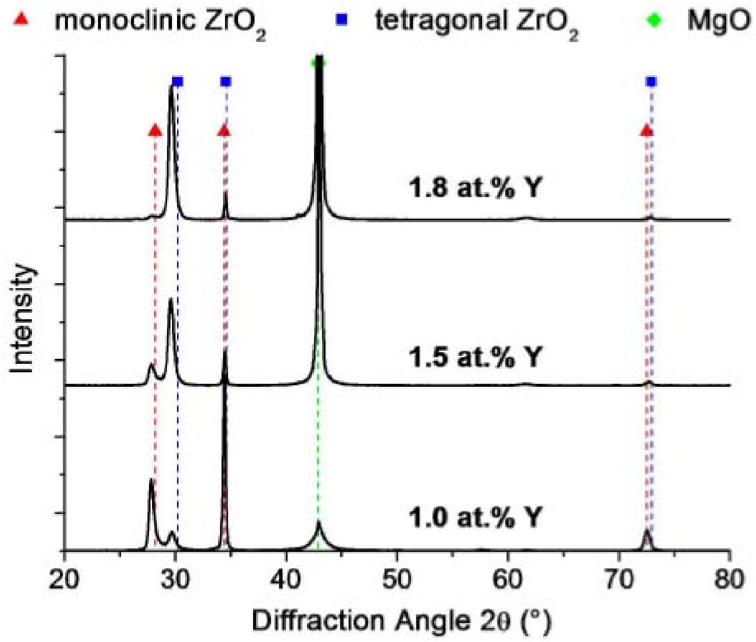

Fig. 2: XRD patterns of ZrO_2 based films with different Y contents grown on MgO (100) substrates.

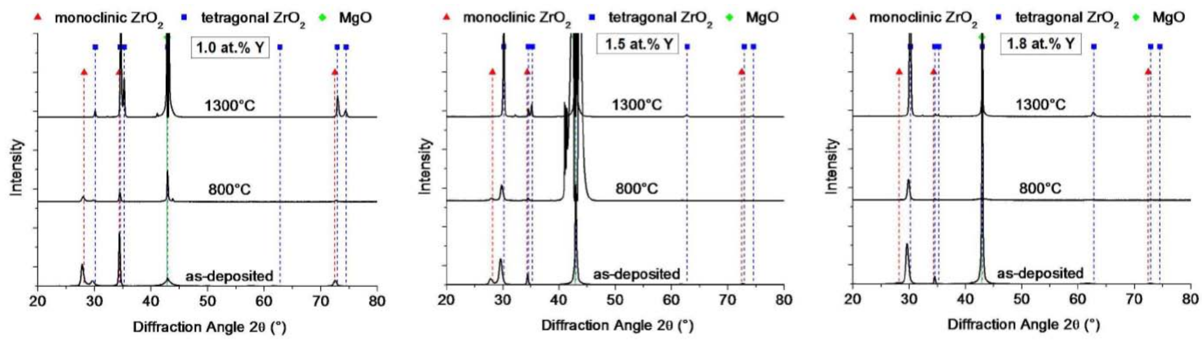

Fig. 3: XRD patterns of ZrO_2 based films with different Y contents grown on MgO (100) substrates after vacuum annealing at 800 and 1300°C for 1 hour.

4.2 Ag alloying of ZrO_2 thin films

While synthesis of ZrO_2 thin films has been done at a substrate temperature of 500°C, it has been reduced to 300°C and 100°C (i.e. the lowest temperature accessible in the sputter system used) to avoid excessive diffusion of Ag. Also at 100°C, the Ag phase is not evenly distributed within the film, but forms clusters and protrusions. Fig. 4 presents an optical micrograph of the surface of a ZrO_2 film with ~10 at.% Ag addition. It can clearly be seen that the surface is covered by Ag agglomerates, which are formed during the deposition process because of the high surface diffusivity of Ag atoms.

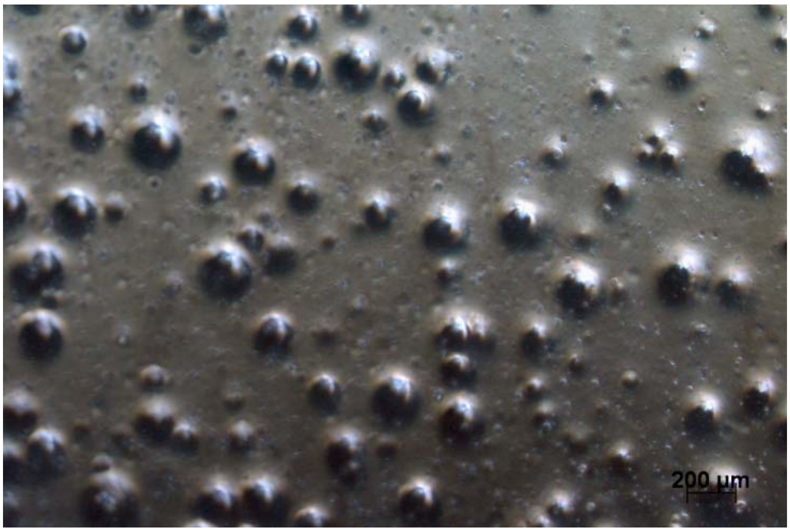

Fig. 4: Optical micrograph of the surface of a ZrO_2 thin film with Ag addition.

Fig. 5 shows the friction curves obtained for the Ag containing ZrO_2 film presented in Fig. 4, where the friction coefficients have been determined by ball-on-disc tests against alumina balls (normal load: 2 N, speed: 10 cm/sec, wear track radius: 6 mm, Al_2O_3 ball radius: 6 mm) in ambient air at different temperatures. At room temperature and 350°C, very similar friction coefficients with values of ~0.5 have been obtained, which indicates that at 350°C no sufficient lubrication due to plastic deformation of Ag takes place. At 700°C, however, the friction coefficient decreases after a short running-in period to a value of ~0.19, which evidences that plastification and eventual melting of the Ag phase in local hot spots takes place. The visual inspection of the sample after tribological testing indicated complete disintegration and delamination of the coating.

In summary, ZrO_2 thin films with Ag additions could be successfully synthesized by magnetron sputtering. However, the mechanical and wear properties of these coatings suffer from the high surface mobility of Ag atoms condensing at the film surface during growth, resulting in formation of Ag clusters and agglomerates. These Ag inhomogeneities are assumed to be responsible for the inferior mechanical coating properties.

4.3 V alloying of ZrO_2 thin films

Within a diploma thesis [2] done within this project, the influence of V on reactively magnetron sputtered non-stabilized zirconia coatings has been investigated with respect to its structural and mechanical properties as well as its thermal management abilities for high temperature sliding interfaces.

ZrO_2 based coatings with three different V contents of 2.2, 5.8 and 17.4 at.% have been synthesized at a substrate temperature of 150°C by reactive unbalanced magnetron sputtering on Si (100), AISI M2 steel and Fe substrates. The tribological performance of these coatings has been compared to undoped ZrO_2 thin films in a temperature range between 25 and 800 °C.

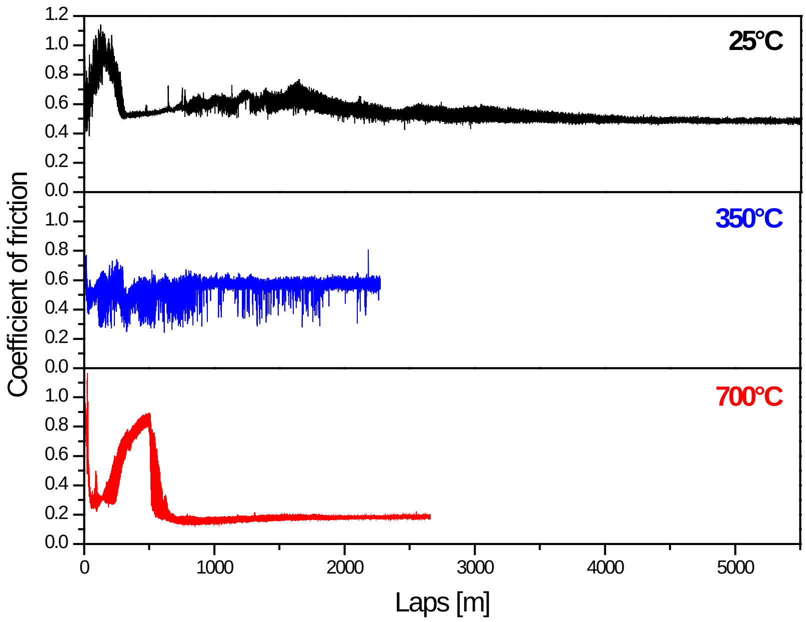

Fig. 5: Friction curves of Ag alloyed ZrO_2 thin films obtained by ball-on-disc tests against alumina balls at room temperature, 350 and 700°C in ambient air (normal load: 2 N, speed: 10 cm/sec, wear track radius: 6 mm, Al_2O_3 ball radius: 6 mm).

The achieved coating thicknesses after 240 - 360 min deposition time are between 1.2 and 2.3 µm with constant surface roughness values for all compositions of about 10±2 nm. The XRD patterns of the as-deposited coatings presented in Fig. 6 indicate a change of the crystal structure of the zirconia matrix with increasing V-content from monoclinic (undoped, 2.2 at.% V) to cubic (5.8 at.% V) and an X-ray amorphous structure (17.4 at.% V), independent of the substrate material used. Since the nature of the V within the coatings could not be illuminated by XRD and Raman spectroscopy, it is assumed that the V is either dissolved within the the ZrO_2 phase or forms an amorphous V-oxide phase.

The maximum stresses are quite low in a range of -400 and 150 MPa. The hardness of the coatings decreases from 17 GPa (constant for V contents up to 5.8 at.%) to 7.4 GPa at 17.4 at.% V. The Young's modulus values display a similar trend as the hardness, decreasing from a value of 220 - 240 GPa (up to a V content of 2.2 at.%) to 152 GPa for the amorphous coating.

The tribological measurements at room temperature indicate friction coefficients of 0.2 and below for the undoped zirconia coating and the one with low V content of 2.2 at.% sliding against alumina balls. The higher the V content is the higher is the friction coefficient and the broader and deeper are the wear tracks. During tribological testing at 600°C, friction coefficients between 0.4 and 0.8 are measured within the first laps followed by coating delamination. After tribological tests at 600 °C, the stoichiometric mixed phase ZrV_2O_7 is detected by XRD (see Fig. 7). This phase is stable up to 750°C and prevents segregation of V_2O_5, and thus no self-lubrication occurs. The formation of ZrV_2O_7 is corroborated by DSC measurements yielding an exothermic peak at 620°C, as shown in Fig. 8. A low friction coefficient of 0.17 is detected at 800°C only for the coating with a V content of 17.4 at.% (see Fig. 9). There, the monoclinic zirconia phase can be assumed to be the mechanically stable phase, providing high wear resistance. The DSC measurements shown in Fig. 8 indicate a strong endothermic reaction at about 670°C, i.e. at the melting point of V_2O_5, which is responsible for the low friction coefficients measured. An additional small endothermic reaction originates from precipitation of V_2O_5 out of ZrV_2O_7. While the exothermic formation of ZrV_2O_7 occurs only during the first thermal cycle (see Fig. 8), the endothermic reactions precipitation of V_2O_5 and melting of this phase take also place during the reruns.

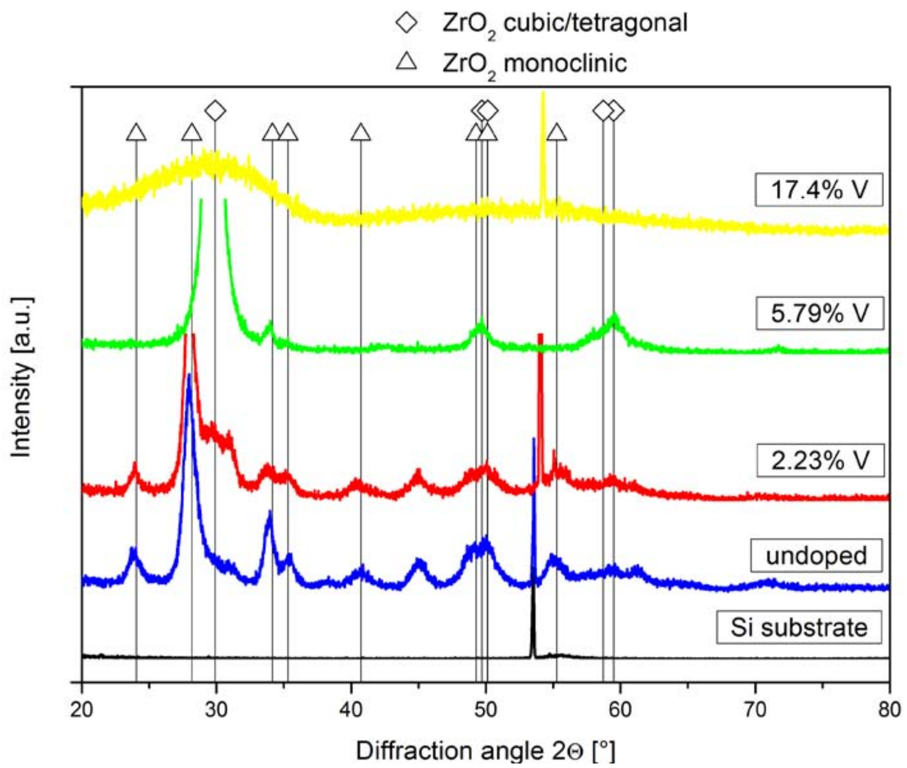

Fig. 6: XRD patterns showing the change of structure from monoclinic to cubic/tetragonal ZrO_2 obtained for ZrO_2 based coatings with increasing V-content on Si (100) substrates.

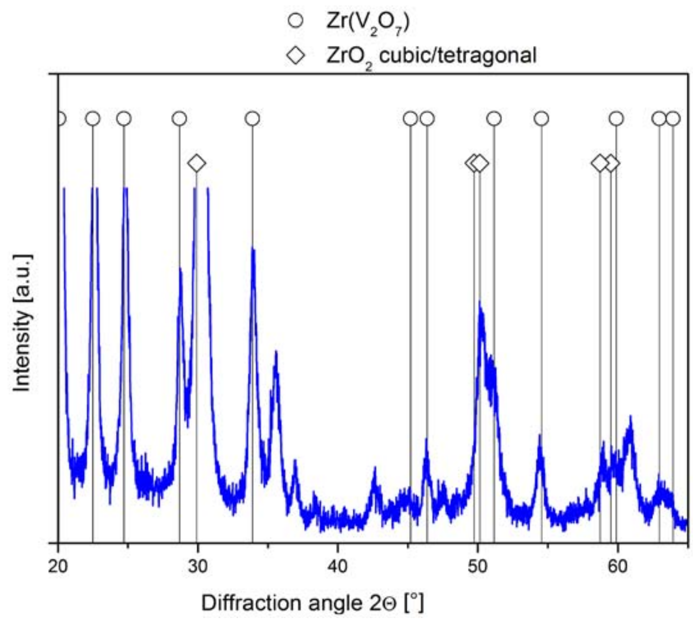

Fig. 7: XRD pattern showing peak positions of ZrV_2O_7 and cubic/tetragonal ZrO_2 after high-temperature tribo-testing of a ZrO_2 coating with 17.4 at.% V at 600 °C in air.

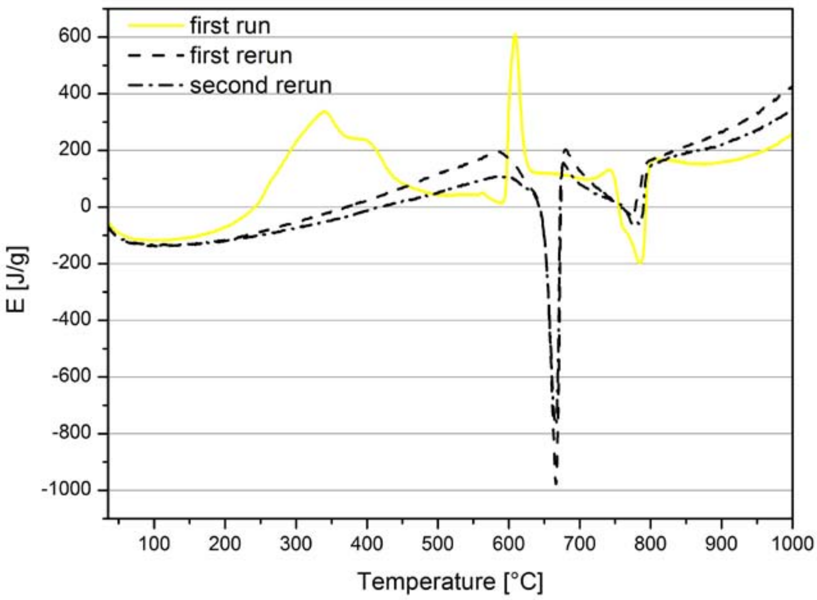

Fig. 8: DSC run of the ZrO_2 coating sample with 17.4 at.% V in synthetic air compared with its first and second rerun showing an endothermic reaction at about 660 °C.

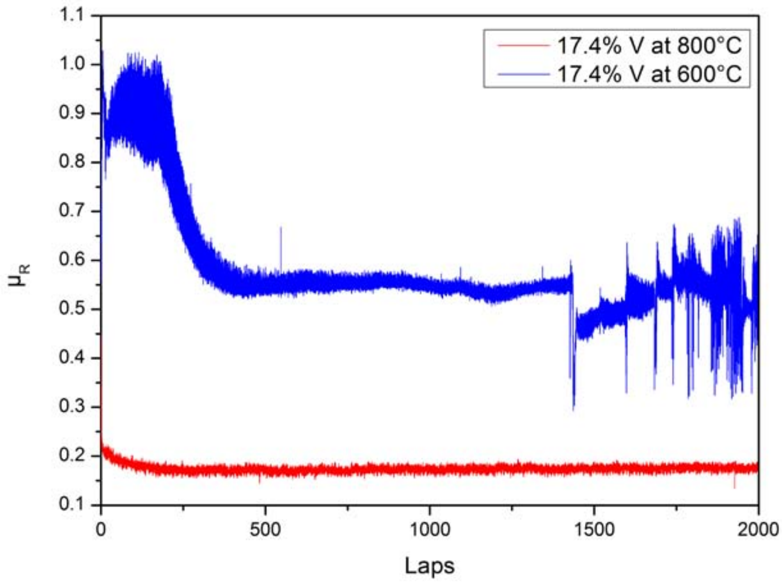

Fig. 9: Friction curves obtained for the ZrO_2 coating with 17.4 at.% V by ball-on-disc tests against alumina balls at 600 and 800°C (normal load: 2 N, speed: 10 cm/sec, wear track radius: 6 mm, Al_2O_3 ball radius: 6 mm).

In summary, it can be concluded that it is possible to achieve self-lubricating behavior in zirconia based coatings with sufficiently high V contents at temperatures of 800°C, where the lubricating molten V_2O_5 phase is formed by an endothermic reaction. This reaction might provide thermal management abilities, by reducing local flash temperatures occurring in sliding contacts. These findings are summarized in more detail in a diploma thesis submitted at the University of Leoben [2], and two publications of the results obtained are presently under preparation [3,4].

5. Summary

Within the present project, three different approaches to synthesize multifunctional low-friction nanocomposite coatings by sputter deposition have been explored, i.e. unalloyed ZrO_2 to investigate the effect of different deposition parameters on phase formation, ZrO_2 films with Ag addition, and finally ZrO_2 films with V addition. The knowledge on controlling phase formation during synthesis of ZrO_2 coatings by magnetron sputtering is the basis for the future exploitation of the stress-induced transformation of metastable ZrO_2 phases and for possible crack-stopping and self-healing mechanisms. While synthesis of Ag containing ZrO_2 films was hampered by formation of Ag clusters and agglomerates, the addition of V allows combining self-lubricious properties with strong endothermic reactions of phase-change materials suitable for reduction of local flash temperatures in tribological hot spots in the temperature range between 600 and 800°C.

The project has contributed to a significant progress in widening the functionality and reliability of nanostructured coatings with added functionalities for highly loaded sliding contacts operated in broad temperature ranges.

6. Publications

1 C. Walter, M. Mühlbacher, C. Mitterer, Control of phase formation during synthesis of ZrO_2 coatings by magnetron sputtering, Poster presentation at International Conference on Metallurgical Coatings and Thin Films, San Diego, CA (USA), 26 April – 1 May 2010.

2 O. Jantschner, Investigation on vanadium containing zirconia coatings for high temperature sliding interfaces, Diploma thesis, University of Leoben, 2010.

3 O. Jantschner, C. Mitterer, C. Muratore, A.A. Voevodin, The effect of V alloying on structure and mechanical properties of ZrO_2 based thin films, in preparation.

4 O. Jantschner, C. Mitterer, C. Muratore, A.A. Voevodin, Low-friction V-alloyed ZrO_2 thin films with temperature homogenization functions for high temperature sliding interfaces, in preparation.